



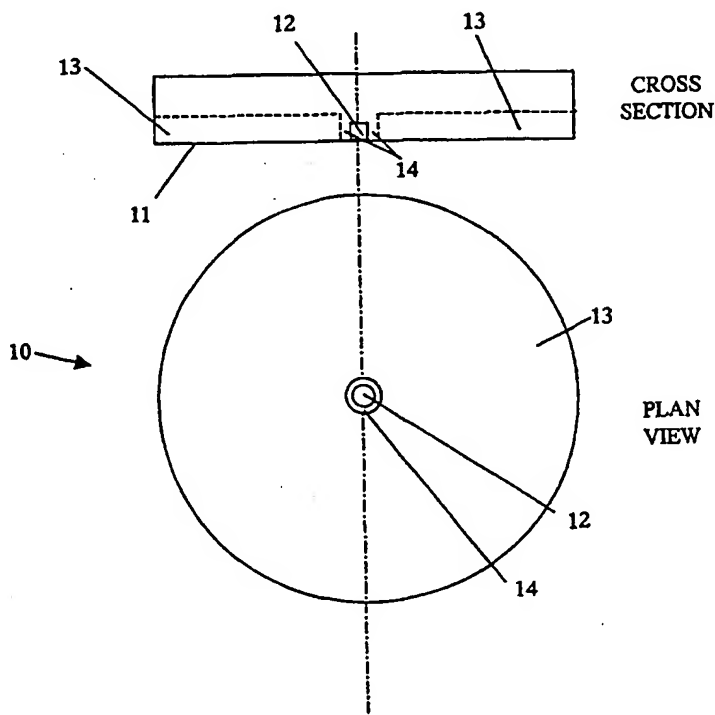
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(54) Title: **THERMAL HISTORY INDICATORS**

(57) Abstract

A temperature history indicator means for affixing to goods. A temperature related phase change in a material within the indicator leads to an indication that a high temperature event has occurred. A preferred format has a water-soluble, lipid-insoluble dye immobilised within a lipid selected to have a melting point at a particular temperature and has all components made from edible materials. Upon melting, the dye dissolves in water present in a secondary phase or the goods themselves giving a visual indication. Another format has a primary reagent within a solid lipid and a secondary reagent held with a secondary phase such that melting of the lipid allows the primary reagent to react with the secondary reagent, providing an indication of a high temperature event. Time-dependent formats are also considered.



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1 THERMAL HISTORY INDICATORS

2

3 The present invention relates to the field of thermal
4 history indicators and time-temperature indicators. These
5 are devices which display a physical change in response to
6 their temperature history and are typically attached to or
7 integrated with temperature sensitive goods in order to
8 provide a quality control and/or quality assurance
9 indicator.

10

11 Many goods sold at the present time are temperature
12 sensitive. For example, fresh food produce needs to be kept
13 in a rigidly temperature controlled environment until it is
14 sold. This has implications for manufacturers, distributors,
15 retailers and consumers.

16

17 Distributors are faced with the technological problem of
18 maintaining temperature of goods within a very tight
19 specification for local, national and international
20 distribution of goods. As a result of this need, it is
21 necessary to verify that goods have been distributed under

1 the required conditions for reasons of quality control and
2 quality assurance.

3

4 Manufacturers and retailers have a duty of care to their
5 customers. When dealing with produce that is temperature
6 sensitive, they must not only control and verify the
7 temperature under which goods are stored and processed
8 internally but will also want to receive proof that raw
9 materials and supplies have been looked after properly.
10 When mistakes in temperature regulation are not noted, goods
11 may be spoiled and unsellable or, worse, may lead to damage
12 to the consumer for which the vendor becomes liable.

13

14 Consumers also face problems related to the temperature
15 control of goods they have purchased. To take an example,
16 milk can spoil extremely quickly if allowed to warm up for a
17 period of time. Consumers would benefit from a way of
18 finding out whether or not retailers are storing goods
19 appropriately. Furthermore, consumers would prefer to
20 purchase goods which they believe have been stored correctly
21 prior to their purchase.

22

23 At the present time, businesses and retailers typically use
24 thermometers and thermocouples to monitor temperature
25 throughout the food chain. Consumers will not usually
26 monitor temperature of their purchases.

27

28 Several organisations currently manufacture and sell time-
29 temperature indicators. These are devices which can be
30 attached to, or be incorporated in packaging and which
31 provide a visual indicator of the temperature history of the
32 label and, therefore, the produce to which it is attached.

1

2 The 3M Monitor Mark contains a dye which moves along a scale
3 when the indicator is above a certain melting point. This
4 suffers from the disadvantages of not being edible, not
5 having a clear link between the length the dye has moved
6 along the scale and the temperature history of the product
7 and also requires to be kept below its freezing point before
8 use.

9

10 The Lifelines Fresh-Check Indicator uses time and
11 temperature sensitive polymers which gradually deepen in
12 colour. The product is considered to be off when an inner
13 ring made of temperature sensitive material becomes darker
14 than an outer ring. This suffers from the disadvantage that
15 the range of thermal sensitivities which the polymer can
16 adopt are not continuous. Usually, different sensitivities
17 are achieved by varying the colour of the printed outer
18 ring. Care is also required by the user when deciding
19 whether the inner or outer ring is darker. This product
20 also requires refrigeration before use and, indeed, must be
21 kept at a particularly cold temperature to ensure that the
22 sensor has not been triggered. Examples of relevant Patents
23 are US 5,709,472; US 4,892,677 and US 4,735,745.

24

25 VITSAB sell time temperature indicators in which an enzyme
26 reaction causes a solution to change from deep green to
27 bright yellow as a result of a controlled pH decrease. A
28 reference colour is printed nearby to enable a viewer to
29 establish whether temperature storage conditions have been
30 violated. One useful benefit of this technology is that the
31 two solutions involved are separated by a divider which can
32 be manually broken, mixing the two solutions (See SE508602

1 and WO9838112). This allows the label to be transported at
2 ambient temperature and to be activated only when it is
3 ready for use. However, this tag is expensive and fragile
4 and may leak; it is not clear whether the enzyme and
5 chemicals involved are entirely non-toxic. Furthermore, as
6 the colour changes gradually, it becomes difficult for a
7 user to judge when the colour has reached the shade of the
8 reference colour.

9

10 These products have so far not been commonly used due to
11 their expense, supply problems with raw materials,
12 limitations to their applicability, toxicity, fragility,
13 sensitivity and the difficulty of manufacture.

14

15 The present invention aims to provide a time-temperature
16 indicator which:

17

18 - is flexible in its application and can be used in many
19 different operating environments;

20

21 - can give a permanent, semi-permanent or non-permanent
22 record;

23

24 - can respond also to the passage of time as well as high
25 temperature events, for example to indicate when a
26 product has been stored too long, even if stored at the
27 correct temperature;

28

29 - is simple to use;

30

31 - is easy and cheap to manufacture and use;

1

2 - is reliable and has reproducible properties;

3

4 - is non-toxic, indeed is actually edible when required for
5 food applications;

6

7 - is adaptable for a plurality of environments;

8

9 - has an expiry recognition system that is adaptable, for
10 instance not simply limited to a colour change;

11

12 - can be adapted to react quickly or slowly to temperature
13 changes; and

14

15 - can be understood regardless of the linguistic base of
16 the user.

17

18 According to a first aspect of the present invention, there
19 is provided a thermal history indicator for attachment to
20 goods, the indicator comprising a temperature sensitive
21 material selected to melt at a predetermined temperature;
22 wherein melting of the temperature sensitive material leads
23 to provision to the user of an indication that the
24 temperature of the indicator has exceeded the predetermined
25 temperature.

26

27 Preferably, the temperature sensitive material is edible.

28

29 Preferably also, the temperature sensitive material is a
30 lipid.

31

1 The temperature sensitive material may provide a visual
2 image through its shape and which melts at the particular
3 temperature, thereby losing its shape, destroying the visual
4 image and thereby indicating that the particular temperature
5 has been exceeded.

6
7 The temperature sensitive material may be mounted on a
8 support, the support being adapted for mounting on goods.

9
10 The indicator may have a chamber within which the
11 temperature sensitive material is held, the chamber being
12 adapted such that the temperature sensitive material
13 obscures a visual indicator and configured such that melting
14 of the temperature sensitive material results in the visual
15 indicator becoming visible.

16
17 Preferably, the chamber is hemispherical and adapted so that
18 the temperature sensitive material flows from the top to the
19 bottom of the hemispherical chamber on melting.

20
21 Preferably, the temperature sensitive material has a primary
22 reagent immobilised therein; the primary reagent is released
23 upon melting of the temperature sensitive material and the
24 released primary reagent provides an indication that the
25 particular temperature has been exceeded.

26
27 The temperature sensitive material may be a lipid, the
28 primary reagent may be a water-soluble dye and the released
29 water-soluble dye may form a colour on contact with water in
30 the goods to which the indicator is affixed, the formation
31 of the colour leading to a visual indication that the
32 particular temperature has been exceeded.

1

2 Preferably, the thermal history indicator has a secondary
3 phase located so that when the temperature sensitive
4 material melts, the primary reagent comes into contact with
5 the secondary phase, wherein contact between the primary
6 reagent and the secondary phase leads to an indication that
7 the particular temperature has been exceeded.

8

9 Typically, the primary reagent interacts with the secondary
10 phase itself in such a way as to produce a colour change.

11

12 Typically, the secondary phase has a secondary reagent held
13 therein, wherein the first reagent and secondary reagent
14 react giving a product which provides a visual indication.

15

16 Typically also, the first and secondary reagents are, in
17 either order, an enzyme and a substrate for the enzyme.

18

19 The temperature sensitive material and the secondary phase
20 may be separated by a physical gap.

21

22 The temperature sensitive material and the secondary phase
23 may be separated by a temperature sensitive barrier.

24

25 The temperature sensitive barrier may have a gate which is
26 opened by a thermostat.

27

28 The temperature sensitive barrier may be a layer of material
29 which melts at a particular temperature.

30

1 The temperature sensitive material and the secondary phase
2 may be separated by a physical barrier which can be broken
3 and thereby made permeable by a user.

4

5 The indicator may have a means for urging molten temperature
6 sensitive material into contact with the secondary phase.

7

8 The thermal history indicator may be configured so that the
9 primary reagent diffuses through the secondary phase,
10 thereby producing a temperature indication that varies with
11 time.

12

13 Preferably, the primary reagent is a water-soluble dye.

14

15 According to a second aspect of the present invention, there
16 is provided a data encoding image comprising a thermal
17 history indicator arranged such that the data encoded by the
18 data encoding image changes when the particular temperature
19 is exceeded.

20

21 Preferably, the data encoding image is a bar code.

22

23 According to a third aspect of the present invention there
24 is provided a temperature history indicator comprising a
25 cylinder, a piston and an indicator which can be viewed
26 through a window, the cylinder having therein a material
27 that changes volume with temperature thereby driving the
28 piston, the piston being linked to the indicator such that
29 motion of the piston is coupled to motion of the indicator,
30 wherein motion of the indicator changes the part of the
31 indicator which can be seen through the window, wherein a
32 first portion of the indicator can be viewed through the

1 window at a first temperature and a second portion of the
2 indicator can be viewed through the window at a second
3 temperature, the first and second portions of the indicator
4 having visually different information thereon and thereby
5 indicating that a temperature change has taken place.

6

7 Preferably, the temperature history indicator is adapted so
8 that motion of the piston is irreversible.

9

10 According to a fourth aspect of the present invention there
11 is provided an indicator for providing temperature sensitive
12 visual images on goods, the indicator comprising lipid
13 formed into a visual image, the lipid being selected to melt
14 above a particular temperature, thereby destroying the
15 visual image.

16

17 An example embodiment of the present invention will now be
18 described with reference to the following Figures in which:

19

20 Figure 1 is a plan view and elevation of a temperature
21 history indicator;

22

23 Figure 2 shows a plan view and elevation of another
24 embodiment of a temperature history indicator;

25

26 Figure 3 shows a plan view and elevation of a further
27 embodiment of a temperature history indicator;

28

29 Figure 4 shows a plan view and elevation of a time-
30 temperature indicator;

31

1 Figure 5 shows a plan view and elevation of a
2 temperature indicator having a thermostat controlled
3 gate mechanism;

4
5 Figure 6 shows a plan view and elevation of a yet
6 further embodiment of a temperature history indicator;
7 and;

8
9 Figure 7 is a graph of phenol red diffusion through
10 agar strips of different agar concentrations and
11 different thicknesses.

12
13 The invention herein disclosed is adapted to monitor
14 temperature-time transformations of products (e.g. foods,
15 pharmaceuticals, hormones, micro-organisms, vaccines,
16 electrical goods, patients, animals), processing techniques,
17 living environments (homes and abodes), working
18 environments, leisure environments, transport, distribution
19 systems etc. The applications are almost limitless and the
20 technology will be of value wherever temperature and time
21 permanent records are required.

22
23 The technology is based around coupling phase transitions of
24 materials to the provision of a record. Phase transitions
25 such as solid to liquid, liquid to gas, solid to gas, liquid
26 crystal to liquid and the like take place at defined
27 temperatures and provide a dramatic change in the structure
28 of a material. Some basic prior art has coupled phase
29 transitions to indicators; for example, a pop-up indicator
30 is disclosed in US 4,356,790 wherein a biased spring moves
31 once a material against which it presses is melted.

1 In the present invention, there are provided a primary
2 reactant which is capable directly or through a reaction
3 with another component, of acting as an indicator.

4

5 In one embodiment, the primary reactant simply disperses
6 when the primary immobilising phase undergoes a phase
7 transitions. In another embodiment, there are two chemical
8 components, the primary and secondary reactants, which can
9 together undergo a chemical reaction which results in a
10 change, such as an colour change, that functions as an
11 indicator. However, the primary reactant is immobilised
12 within a material, known as the primary immobilising phase,
13 and thereby kept separate from the secondary reactant until
14 such time as the primary immobilising phase undergoes a
15 phase transition which releases the primary reactant. The
16 secondary reactant may simply be water; for instance, a
17 dyestuff may be used as primary reactant which is colourless
18 in a lipid-based primary immobilising phase but has colour
19 when in contact with water (the water acting as secondary
20 reactant or secondary immobilising phase).

21

22 The primary immobilising phase is chosen to undergo a phase
23 transition at a desired temperature and/or to otherwise
24 break down and release the primary immobilising phase with
25 time. The phase transition may for example be melting,
26 sublimation, evaporation, formation or breakdown of liquid-
27 crystal phase etc. The preferred transition is melting.
28 The secondary reactant may also be immobilised in a
29 secondary immobilising phase.

30

1 When the primary and secondary reactants meet and undergo a
2 reaction, a colour, smell or other indicator is provided
3 that can be sensed by an observer.

4
5 Considerations relating to the primary immobilising phase,
6 secondary immobilising phase (if present) and indication
7 mechanism will now be presented in turn, followed by more
8 detailed examples.

9
10 Primary immobilising phase

11
12 A key development in the present invention is the use of
13 lipids as the primary immobilising phase (PIP). Although
14 any appropriate material with defined (sharp or broad) phase
15 transitions may be used (e.g. waxes and hydrocarbons), data
16 and experimental results disclosed herein show that lipids
17 are ideal materials for use in time-temperature indicators
18 for two important reasons. Firstly, a great many different
19 lipids can be readily purchased or manufactured with
20 different melting points. Therefore, it is easy to tune the
21 trigger temperature of the system by selecting a different
22 lipid. Secondly, lipids are safe to use and are generally
23 edible. Further benefits are that they are readily and
24 cheaply available, can be readily modified and derivatised,
25 have physical and chemical characteristics compatible with
26 time-temperature indicators and are hydrophobic.
27 Hydrophobicity is of great benefit as, in an indicator
28 format in which the secondary reactant is kept in an aqueous
29 phase, the primary immobilising phase will not dissolve nor
30 readily allow unwanted mixing of the primary and secondary
31 reactants.

1 Because of the normal operating environments for this
2 technology and their broad range of chemical and physical
3 properties and safety, lipids (fats, oils, conjugates,
4 mixtures of etc.) and their derivatives are extensively used
5 (singly or mixtures) herein. Within this document and the
6 appended claims, the term lipid includes all waxes, esters
7 of fatty acids, simple and compound lipids. Upon melting,
8 the primary reactant (PR) or reactants (PRs) are released.
9 The PR can itself be the indicator of change or can further
10 react with another component (below). Table 1 shows the
11 melting temperatures of example hydrocarbons and similar
12 organic molecules, which although not all lipids, could be
13 used as PIPs with melting transitions from around 0 to 20°C.
14 Table 2 shows the equivalent properties of fatty acids.

15

16 Table 1. Examples of PIPs - Melting Transitions from around
17 0 to 20°C

18

Compound	Melting Temperature (°C)
1-bromotetradecane	4.5
1-bromotridecane	6.0
2-cyclopentene-6-tridecenoic acid	6.0
5-decanol	8.7
1,13-dibromotridecane	8-10
6-dodecanone	9
5-dodecenoic acid	1-1.3
Glycerol 2-9, 12-octadecadienoate	8.9
9-henicosene	3
1-hexadecene	4.1

2-methylheptadecane	5.7
6-methylheptanoic acid	0
Methanoic acid	8.4
Methyl dodecanoate	5.1
Methyl tridecanoate	5.8
2-nonenoic acid	0.3
8-nonenoic acid	5
11,14-octadecadienoic acid	4.5-5.5
9-octadecen-2,4,6-triynedioic acid	0
9-octyl-9-heptadecanol	8-9
2-(octylthio)ethanol	0
Methyl 5-oxodecanoic acid	5
Tetradecane	5.9
6-tridecynoic acid	7.5-8.5
Tridecane	-5.5
Tetradecane	5.9
Pentadecane	10
Hexadecane	18.2
2,5-undecadiyn-1-ol	1.2-1.5
4-undecanone	4-5
5-undecanone	2

1

2 Table 2. Examples of PIPs - Fatty Acid Melting Points

3

Systematic Name of Fatty Acid	Fatty Acid mp (°C)	Methyl Ester mp (°C)
Methanoic	8.4	-
Ethanoic	16.6	-
Propanoic	-20.8	-

Butanoic	-5.3	-
Pentanoic	-34.5	-80.7
Hexanoic	-3.2	-69.6
Heptanoic	-7.5	-55.7
Octanoic	16.5	-36.7
Nonanoic	12.5	-34.3
Decanoic	31.6	-12.8
Undecanoic	29.3	-11.3
Dodecanoic	44.8	5.1
Tridecanoic	41.8	5.8
Tetradecanoic	54.4	19.1
Pentadecanoic	52.5	19.1
Hexadecanoic	62.9	30.7
Heptadecanoic	61.3	29.7
Octadecanoic	70.1	37.8
Nonadecanoic	69.4	38.5
Icosanoic	76.1	46.4
Henicosanoic	75.2	-
Docosanoic	80.0	51.8
Tricosanoic	79.6	53.9
Tetracosanoic	84.2	57.4
Pentacosanoic	83.5	59.5
Hexacosanoic	87.8	63.5
Heptacosanoic	87.6	64.6
Octacosanoic	90.9	67.5
Nonacosanoic	90.4	68.8
Tricontanoic	93.6	71.5

1
2 When for example glycerides are used, depending on the
3 crystalline form, there are different melting points as
4 shown in Table 3.

Table 3. Examples of PIPs - Monoglyceride Melting Points

Glycerol-1-alkanoate	Mp β ($^{\circ}\text{C}$)	Mp β' ($^{\circ}\text{C}$)	Mp α ($^{\circ}\text{C}$)
Decanoate	53	49	27
Undecanoate	56.5	52	36.5
Dodecanoate	63	59.5	44
Tridecanoate	65	61	50
Tetradecanoate	70.5	67.5	56
Pentadecanoate	72	69	62
Hexadecanoate	77	74	66.5
Heptadecanoate	77	74.5	70
Octadecanoate	81.5	79	74

A broad range of melting points similarly exists for di- and triglycerides - which are equally valuable for this technology.

Table 4. Examples of PIPs - Triglyceride Melting Points

Chain length	Melting Point ($^{\circ}\text{C}$)			Long Spacing x 10^{-10}m		
	α	β'	β	α	β'	β
8	-51.0	-18.0	10.0	-	-	22.7
9	-26.0	4.0	10.5	-	25.3	24.9
10	-10.5	17.0	32.0	30.2	27.7	26.5
11	2.5	27.0	31.0	32.7	29.8	29.6
12	15.0	34.5	46.5	35.6	32.9	31.2
13	24.5	41.4	44.5	37.8	34.2	34.0
14	33.0	46.0	58.0	41.0	37.3	35.7
15	39.0	51.5	55.0	42.9	39.2	39.2

16	45.0	56.5	66.0	45.8	42.5	40.8
17	50.0	60.5	64.0	48.5	43.8	43.5
18	54.7	64.0	73.3	50.6	47.0	45.1
19	59.0	65.5	71.0	53.1	48.1	48.2
20	62.0	69.0	78.0	55.8	50.7	49.5
21	65.0	71.0	76.0	58.5	53.2	52.7
22	68.0	74.0	82.5	61.5	56.0	54.0

1

2 Other phase transitions associated with other materials are
3 not, however, excluded. An alternative example would use
4 solvents (e.g. water) or solutions in which the particular
5 solutes defined the melting point.

6

7 Many different lipid systems have been investigated as the
8 melting phase. Fatty acids, monoglycerides, diglycerides and
9 triglycerides are all effective. Care must be taken to
10 retain the appropriate crystalline form (especially the di
11 and triglycerides).

12

13 Mixtures of lipids, non-lipids and lipids with non-lipids
14 are also envisaged for the PIP. These may/may not include
15 other non-lipid components.

16

17 Secondary immobilising phase

18

19 In embodiments where there is a secondary reactant (SR), a
20 secondary immobilising phase may be provided. The secondary
21 immobilising phase (SIP) can be any material which can form
22 a matrix to entrap the secondary reactant (SR) or reactants
23 (SRs).

24

1 The secondary immobilising phase is often solvent based.
2 Although lipids may form the matrix, typically a permeable
3 matrix is used which entraps water. For example polymer
4 based materials can be used, where polysaccharide based
5 materials are preferred because time dependent
6 biodegradation of these materials can be built in if
7 desired(discussed further below).

8

9 A broad range of polymeric - especially polysaccharide
10 systems - have been evaluated for this phase. A readily
11 gelling phase is preferred that can readily entrap a
12 solvent/solution with a small polysaccharide to
13 solvent/solution ratio. Mixtures of these polymers, their
14 derivatives and hydrolysis products are also valuable.
15 Protein gels (like gelatine) work well, although potential
16 problems with BSE favour the use of other gelling materials
17 from plants in particular - like polysaccharides.

18

19 Alginic acid, pectin, starch and agar gels have been used
20 successfully, although other polysaccharides can equally be
21 used. Mixtures can also be used. Agar forms very rigid gels,
22 can entrap large volumes of water and other materials, can
23 be blended with for example gelatinised starch, can be
24 sterilised and can contain antimicrobiological agents.

25

26 A preferred embodiment uses a lipid as primary immobilising
27 phase and a water containing medium as secondary
28 immobilising phase wherein the primary reactant is a water
29 soluble chemical trapped within the primary immobilising
30 phase.

31

1 In several of the examples given below, agar gel is
2 preferred as secondary immobilising phase. When using a
3 gel, the choice of material is important. Agar poorly
4 withstands freeze-thaw cycles (largely independently of
5 concentration), as syneresis occurs. In circumstance where
6 there may be multiple freezer-thaw incidents, it is
7 preferable to use other polysaccharides like iota
8 carrageenan, locust bean and xanthan gums. These we have
9 found to be very successful.

10

11 Indication mechanism

12

13 The main trigger which activates the indicator is melting of
14 the PIP. Phase transition of this phase (typically melting,
15 i.e. a solid-liquid transition) releases the reactant which
16 leads to a permanent irreversible change that functions as
17 an indicator. This can be a colour, smell, texture
18 difference etc. If, for example, a lipid is used it can melt
19 and liberate a dye/colour. In a preferred embodiment, non-
20 lipid soluble colours are used which have little colour when
21 particulate in the lipid PIP but are coloured once dissolved
22 in an aqueous SIP. A PR is chosen which can freely dissolve
23 in whatever SIP is chosen.

24

25 Although the PR may be a dye or indicator, it may be any
26 chemical species. This can further react with another
27 compound or compounds to indicate a permanent and preferably
28 irreversible change.

29

30 The PR may also be a biochemical species like an enzyme or
31 enzyme substrate or a biologically important molecule like
32 a protein, lipid, carbohydrate, mineral, vitamin or element.

1

2 The PR could be a micro-organism, cellular structure or
3 organism or a substance metabolised by these living species
4 (for example a sugar which could be metabolised by a yeast
5 and coupled to a colour change). A micro-organism could be
6 released on melting of the PIP and then grow, with the
7 growth coupled to a colour change reaction by techniques
8 known to those skilled in the art.

9

10 The PR may itself be a solvent (like water) and the PIP may
11 be in the form of an emulsion.

12

13 The PR may also be particulate or made from materials such
14 as to create a particular structure which is obvious as a
15 consequence of PIP passing through a phase transition.

16

17 The PR may be a volatile material which is entrapped by the
18 PIP. For example an odorous material which is only obvious
19 upon phase transition of the PIP.

20

21 The SR may be an immobilised solvent (e.g. water), solution,
22 colloid or suspension. Equally, the SR may be one or more
23 of: chemical; molecule; biochemical (including enzymes and
24 substrates); organism, microorganism or tissue or substrate
25 thereof in some combination.

26

27 Application One

28

29 The simplest application of this technology is to monitor
30 defrosting, warming and heating of products such as meat,
31 meat products, poultry etc., although any food,
32 pharmaceutical, apparatus, environment etc. would be

1 appropriate. In this example, the indicator is applied
2 directly to the actual product to be monitored.

3

4 An appropriate lipid or suitable edible or non-edible
5 material is chosen as PIP with the desired melting point. If
6 for example the transition through 13°C is required, oleic
7 acid is appropriate.

8

9 A fat insoluble or soluble dye (or appropriate material) is
10 used as PR and is blended into the lipid. No SIP or SR is
11 required. The preferred option is to use a fat soluble food
12 dye which forms a particulate nature when dispersed in fat.
13 This can then be applied directly to frozen meat (spray,
14 stamp, print etc) in the form of lettering or shapes. If
15 oleic acid is used on frozen meat etc., it instantly freezes
16 and the letter/shape is permanent until the sausage
17 defrosts. Therefore, a visible indicator which may be even
18 be words, such as "SAFE" can be displayed harmlessly on the
19 product and will be destroyed when the temperature of the
20 produce exceeds the melting temperature for a significant
21 period of time.

22

23 In a related embodiment, an organisation's brand or any
24 other sort of identifier or advertising could be written
25 directly onto a product such as a meat, but disappear during
26 the cooking process as it melts.

27

28 Alternatively, a thin film of the lipid is applied to the
29 cut of meat etc. below this temperature, the lipid remains
30 intact as a thin film. If the meat is frozen, it is very

1 easy to stamp or brush a small film of the lipid onto the
2 meat directly.

3

4 In practice, we have found this to work effectively and well
5 with the following three approaches being particularly
6 successful for, by way of example, applying triglycerides as
7 melt indicators on the surface of meat products such as
8 sausages. It is important to be careful not to modify the
9 crystalline structure of the lipid in a manner which
10 undesirably alters the lipid melting characteristics.

11

12 • Melting and stamping

13

14 • Dissolving in appropriate solvent - hexane was especially
15 valuable

16

17 • Dispersing in a 'gluing' medium. Polysaccharides and
18 gelatine are especially valuable in this respect.

19

20 If the meat is wet, the lipid film can be stamped, brushed
21 etc. onto an edible base - rice paper is preferred. Onto
22 this base, another thin film is applied but this time the
23 film contains an/the indicator which may be an edible
24 material (like food colour, above) which becomes obvious
25 when the trigger temperature has been exceeded. If printed
26 on the rice paper, the sandwich disc is then applied to the
27 meat. The transition may be a visible transformation, a
28 smell (i.e. a volatile compound is entrapped), a texture
29 etc. Lettering or shapes printed using the lipid-dye mixture
30 on the rice paper lose their image upon melting providing a
31 useful indication that the product is no longer safe to eat.

1

2 Food colours have been found to be particularly suitable as
3 PR in this application as they are freely water-soluble and
4 form small particles within the lipid phase without any
5 discernible colour.

6

7 When the meat is heated, the lipid melts and the food colour
8 interacts with the water from the meat and a visible smear
9 is obvious. The meat can of course be eaten without any harm
10 from the indicator, although the indicator shows that it has
11 been heated above a safe storage regime.

12

13 Example 1

14

15 To 1g of oleic acid at room temperature (where it is a
16 liquid), 10mg of patent blue was added. The dye was
17 dispersed by thorough mixing whereupon the particles are
18 dispersed throughout the lipid. Shapes and letters were
19 drawn and written onto frozen sausages, frozen burgers and
20 egg shells for eggs previously stored in a refrigerator. The
21 mixture rapidly solidifies on the surface and can be happily
22 stored in the freezer (meat) or refrigerator (egg) without
23 any change. However, upon defrosting, the lipid melts and
24 the image is lost. In addition, the food dye stains the meat
25 (blue) indicating that it has defrosted. It has to be noted
26 that this is a natural event when the food is legitimately
27 defrosted for food use, and the food can be eaten as normal.

28

29 For foods that are refrigerated, the rice paper disc
30 approach is most appropriate and can successfully indicate a
31 temperature transition. Using the same lipid and dye, the
32 defrosting of burgers has been successfully monitored.

1

2 Example 2

3

4 Discs of rice paper were soaked in oleic acid and the excess
5 lipid was drained away. The discs were cooled to 5°C. To the
6 surface of this phase, shapes (or lettering) of oleic acid
7 containing patent blue (as above) were applied. Many
8 technologies can be used for this purpose, e.g. painting,
9 stamping, spraying, ink jet printing. The discs were cooled
10 and then placed on the surface of sausages and burgers
11 within the refrigerator. Nothing happens until the meat
12 products are removed from the cool environment, whereupon
13 the lipid melts and a permanent record of the thermal
14 exposure is obvious.

15

16 Example 3

17

18 Commercial triglycerides were obtained from a number of
19 suppliers. Two products, one with a peak melting temperature
20 (established by differential scanning calorimetry) of -65°C
21 and another with a peak melting temperature of -74°C were
22 applied to food products including sausages. Application was
23 achieved in three ways:

24

25 By dissolving in solvent (especially hexane) and applying
26 the solution in a form of a shape to the surface of the
27 sausage. Reactants like dyes were also applied to the
28 sausage surface in this way, where they were immobilised in
29 the lipid. The sausages were heated at different
30 temperatures and the core temperature was monitored with
31 respect to melting of the surface lipid layer. Colony counts
32 of surface and core microorganisms were also made as a

1 function of the cooking time. These data are presented in
2 the following tables:

3

4 Table 17 - Average core temperature of collagen cased
5 sausages cooked at 100°C for up to 1.20 hours in a
6 convection oven

7

Time (mins)	Average core temperature (mean of 2)
10	44.5
20	68
30	84.5
40	84
50	88.5
60	92
70	94
80	97

8

9

10 Table 18 Average core temperature of collagen cased sausages
11 cooked at 80°C for up to 3 hours in a convection oven

12

Time (mins / hours)	Average core temperature (mean of 2)
10 mins	27.5
20 mins	41.5
30 mins	47.5
40 mins	59.5
50 mins	63.5

1 hour	63
1.10 hours	70.5
1.20 hours	70.5
1.30 hours	70.5
1.40 hours	74
1.50 hours	75.5
2.00 hours	78
2.10 hours	78.5
2.20 hours	78.5
2.30 hours	79.5
2.40 hours	79.5
2.50 hours	80
3.00 hours	80

1
2 Table 19 - Average core temperature of collagen cased
3 sausages cooked at 100°C for up to 1 hour in a convection
4 oven

5

Time (mins)	Average core temperature (mean of 2)
10	53
20	67
30	80
40	80
50	89.5
60	89

6

7 Bacterial Analysis of Sausages

8

9 10 g sample was taken into 90 ml diluent. Serial dilutions
10 were made (1:10 to 1:10000), and duplicate plates were made.

1

2 Before cooking:

3

4 Dilution 1:100 was selected

5 Number of colonies / plate 297 and 44

6 The average 171

7 Therefore $171 \times 10 \times 100 = 171000$ CFU/g

8

9 After cooking: (after 30 mins)

10 (Internal temperature 80°C)

11

12 Dilution 1:10 was selected

13 Number of colonies / plate 46 and 36

14 The average 41

15 Therefore $41 \times 10 \times 10 = 4100$ CFU / gram

16

17 The number of bacteria dropped sharply after sausages were
18 cooked at 100°C for about 30 mins. The availability of
19 bacteria in the cooked sausages was due to the fact that no
20 food is free from micro-organisms unless the food is
21 sterilised to over 121°C for at least 15 mins.

22

23 Table 20 - Average times when fat was melted on sausages
24 cooked at 80°C in a convection oven

25

	Average time (mins)	Remarks
Fat in test tube	10	Fat started melting
Melted fat on	25.5	at 8 mins
sausage		Fat started melting
Fat in solvent on	32.5	at 20 mins
sausage		Solvent evaporated

Fat in solvent in tube	5.5	at 13 mins Fat started melting at 30 mins
------------------------	-----	-------------------------------------------------

1

2

3 Table 21 - Average times when fat was melted on sausages4 cooked at 100°C in a convection oven

5

	Average time (mins)	Remarks
Melted fat on sausage	11	Fat started melting at 8 mins
Fat in solvent on sausage	12	Fat started melting at 10 mins
Fat in gelatine on sausage	16	Fat started melting at 12 mins

6

7

8 Table 22 - Time when fat melted on sausages cooked at 100°C9 in a convection oven. The fat was mixed with solvent,10 starch, carrageenan and gelatine

11

	Average time (mins)
Fat in solvent on sausage	19
Fat in starch on sausage	20
Fat in carrageenan on sausages	20
Fat in gelatine on sausage	20

12

13

1 Table 23 - Time when fat with starch and gelatine at
2 different concentrations were melted on cellulose cased
3 sausages cooked at 100°C in a convection oven

4

	Conc (%)	Average time (mins)
Starch on sausages	3	18
	4	24
	5	25
Gelatine on sausages	3	22
	4	22
	5	18

5

6 These results show that lipid applied directly to the
7 surface of sausages can be used to provide visible images
8 which are destroyed by heating in conditions appropriate for
9 the safe cooking of sausages.

10

11 Example 4 - process monitoring.

12

13 The technology described above can also be adapted to
14 monitor temperature transfer in food products to assess the
15 effectiveness of processing operations (and related
16 industrial processes).

17

18 Small wells are created within little block of high melting
19 temperature fats. A paste of lipid (which may be the same
20 lipid as the block of high melting temperature fat or a
21 different material) containing food colour (e.g. patent
22 blue) was inserted. Into the recess of the small blocks,
23 colouring free lipid was applied. These fat blocks were
24 placed in raw meat pies and the pies were heated. Upon

1 cutting open, only those pies exposed to temperatures above
2 the melting point of the lipids contained dye stains -
3 showing where temperature penetration occurred.

4
5 Note that lipid mixtures and mixtures with other products
6 (e.g. carbohydrates, proteins etc) can also be used for this
7 purpose.

8
9 Example Five

10
11 Figure 1 shows a plan view of and cross section through an
12 indicator according to the present invention. An indicator
13 1 comprises an enclosure 2 with transparent bubble-shaped
14 window 3 within which there is frozen lipid 4. Coloured
15 card 5 makes a backing. When the lipid 4 melts, it runs
16 down from the bubble shaped window 3, revealing the coloured
17 card which indicates there has been an overtemperature
18 event. The lipid is absorbed into absorbent material 6
19 thereby preventing it reobscuring the card. Importantly,
20 this construction will function at all orientations.

21
22 Application Two - Packaging type temperature transition
23 indicators.

24
25 In this application, temperature transition indicators
26 adapted for application to packaging of temperature
27 sensitive items is disclosed.

28
29 Example Six

30
31 A dyestuff, Patent blue (10mg), was added to 1g of oleic
32 acid (although other appropriate lipids, combinations,

1 mixtures etc. can be used) at room temperature (where oleic
2 acid is a liquid). The particles are dispersed throughout
3 the lipid by thorough mixing. The dye/food colour must be
4 water but not fat soluble, since this means that no obvious
5 colour is apparent in the lipid but simply discrete
6 particles.

7

8 Into small plastic petri-dish type plates, 1% agar solutions
9 were poured. Gelatine and other polysaccharide systems were
10 also found to be effective, as were polysaccharide mixtures.
11 The agar simply serves as an example. Agar was removed from
12 the centre of the agar plates, and the plates were then
13 cooled below 5°C.

14

15 Small volumes of the lipid containing the water soluble dye
16 were pipetted into the agar free region of the petri dishes.
17 The lipid cools on contact with the cold dish. The plates
18 were immediately refrigerated whereupon the lipid was
19 immobilised. In this embodiment, a physical gap separates
20 the dye containing lipid from the agar.

21

22 As well as circular set pools of lipid, other geometric
23 forms can and have been readily produced.

24

25 In an alternative embodiment, lipid without dye is pipetted
26 into the agar free region. When cooled and solidified, a
27 well is made in this lipid and lipid containing the dye is
28 pipetted into this well. In this embodiment, the dye-free
29 lipid forms an interface layer between the dye containing
30 lipid and the agar.

31

1 In both embodiments, the lipid containing the water soluble
2 dye is solidified. It is separated from the agar either by a
3 physical gap or an interface which acts as a physical
4 barrier and responds to temperature. The preferred method
5 is to use a lipid as an interface layer.

6
7 In all systems, when the melting point of the lipid is
8 exceed, the lipid containing the water soluble dye melts and
9 runs into the agar. The dye diffuses into the agar and the
10 colour becomes obvious. Any colour may be used provided that
11 it is water soluble.

12
13 The rate of colour development throughout the agar is time
14 dependent and can be modified by the gel composition -
15 including agar concentration, adjuncts etc.

16
17 The benefit of this approach being that if the dye
18 containing lipid is placed next to the agar (which contains
19 99% water), although the lipid has not melted, the dye still
20 diffuses from the lipid into the agar and generates a
21 colour. Hence, instead of relying upon a gap in space to
22 separate the agar from the dye containing lipid, a dye free
23 lipid interface can be used very effectively. This has been
24 especially useful when making laminates of the technology
25 where the agar layer is coated with dye free lipid and
26 cooled to solidify the lipid. To the lipid layer, a lipid
27 layer containing water soluble dye is painted and the system
28 is cooled. Hence no interaction between the lipid containing
29 the dye and the agar can occur because of the lipid
30 interface.

31

1 The interaction of lipid and agar can also be optimised by
2 design - for example by applying the lipid to a small mound
3 on the dish which forces the lipid-dye mixture to run
4 towards the agar when melted.

5
6 To extend the life of the agar, it is necessary to use
7 preservatives as it gets readily infected by bacteria and
8 moulds. Alternatively, sterile production may be employed.

9
10 An example implementation is shown in plan and cross-
11 sectional views in Figure 2. Indicator 10 consists of a
12 petri dish 11 which has a block of lipid 12 containing a
13 water-soluble, lipid-insoluble dye. Agar gel 13 surrounds
14 the lipid block separated by, in this example, a physical
15 gap 14. A preferred embodiment would use a dye free lipid
16 layer. Upon raising to a temperature where the lipid block
17 12 melts, the dye is released into the agar gel, becoming
18 visible.

19
20 Figure 3 shows an improved embodiment in plan view, cross-
21 section and end view before the final construction stage.
22 Sensor 20 is made from a base 21 to which is clipped a cover
23 22, using clips 23. Lipid block 24 is positioned so that
24 when it melts, lipid runs onto spike 25 and thereby into
25 contact with agar blocks 26 where indication takes place as
26 above.

27
28 Example Seven - use of chemical reaction to enhance
29 indication.

30
31 The dye diffusion as described above is 'passive' diffusion
32 of a water soluble dye into water (in the agar) to generate

1 colour. The resulting (typically visual) indication can be
2 enhanced and made more striking by designing a system
3 wherein the primary reactant reacts with a secondary
4 reactant present in a secondary immobilising phase.

5
6 Agar as secondary immobilising phase has also be produced
7 containing 1-5% sodium bicarbonate or containing given
8 molarities of sodium hydroxide as secondary reactant. In
9 place of the patent blue in the lipid, phenol red, cresol
10 red, phenolphthalein (typically 1%) and other pH indicators
11 have been used as primary reactant. These readily develop a
12 colour upon the contact with the alkali in the agar after
13 the primary immobilising phase (the lipid) has melted. Other
14 chemical colour generating systems have been employed where
15 one reactant resides in the agar and one in the lipid.
16 Systems responsive to pH, silver nitrate interacting with
17 chloride systems, acid (e.g. HCl) reacting with bicarbonate
18 to generate carbon dioxide, dye binding of protein etc. have
19 been evaluated. Other systems are not excluded.

20
21 The pH sensitive systems are especially attractive in view
22 of the different colours that can be easily formed. This
23 effect can be multiplied by using different indicators in
24 different lipids (with different melting points).

25
26 The key to this approach is, therefore, the provision of a
27 water soluble reactant (which may only be water) acting as
28 secondary reactant in the agar phase (secondary immobilising
29 phase) and a water soluble reactant acting as primary
30 reactant (which may just be a dye) in the solidified lipid
31 (primary immobilising phase). The two reactants meet upon
32 lipid melting.

1
2 The version of the system where a circle of agar surrounds a
3 lipid containing dye (with perhaps a dye free lipid
4 interface rather than a gap) is easy to manufacture.
5 However, the laminate approach is easier still to prepare.
6 These are made as follows:

7
8 Pour an agar plate (1% with respect to agar and sodium
9 bicarbonate) about 0.5mm thick. Immediately cool to 5°C.
10 Onto this apply a thin film of oleic acid - which freezes
11 immediately as the agar is less than 5°C. The oleic acid may
12 be painted on, although it is easier to spray it uniformly.
13 Immediately cool to 5°C. Onto this solid lipid film apply a
14 thin film of oleic acid containing 1% cresol red- which also
15 freezes immediately as the lipid interface and agar base are
16 less than 5°C. When the system is placed at room temperature
17 both lipid phases melt and the dye comes into contact with
18 the agar and a red colour develops.

19
20 In a trial, Agar plates (1%) containing water or 1% sodium
21 bicarbonate are prepared. From the centre small holes were
22 cut in the agar and oleic acid (mp 13.4°C) containing congo
23 red dye, cresol red or phenolphthalein.

24
25 No colour generation within the agar was identified upon
26 storage at 5 or 10°C. However at 15°C there was slow
27 generation of colour (<5 minutes). At 25°C this was very
28 fast (<1 minute).

29
30 The polysaccharide gels (variable concentrations) made of
31 water and polysaccharide or containing alkali (like 1%
32 sodium bicarbonate) were stored at refrigeration temperature

1 for up to sixteen weeks and were found to exhibit no change
2 in performance with respect to their ability to operate in
3 the time-temperature devices.

4
5 Clearly, the embodiments of Figures 2 and 3 can be used to
6 apply this example in practice.

7
8 Example Eight

9
10 This Example details a biochemical approach where an enzyme
11 or substrate as primary reactant is immobilised in a lipid
12 primary immobilising phase, with a secondary reactant which
13 undergoes a reaction with the primary reactant in the agar.

14
15 In one experiment, mushrooms were purchased from a local
16 shop and freeze dried. The mushrooms were then pulverised to
17 a powder and dispersed throughout oleic acid. Agar (1%) was
18 prepared containing 1% tyrosine and the indicators were
19 configured as described above. Upon melting, the
20 polyphenoloxidase (PPO) from the mushrooms reacts with the
21 tyrosine in the agar and generates a pink colour. This
22 embodiment contains only edible materials and so is likely
23 to be well regarded by the public. The functionality has
24 been further confirmed using commercial PPO.

25
26 Hence, as well as the chemical-chemical indication system
27 described above, a biochemical approach can also be used.
28 These can essentially be any enzyme-substrate processes that
29 provides a suitable indication.

1 It will be clear to one skilled in the art that
2 immunological systems and diagnostic systems may be made
3 using the same approach.

4

5 Microorganisms (MOs) have also been immobilised in the lipid
6 phase. Upon melting the MOs come into contact with the agar
7 phase and may thereupon grow and as a consequence produce
8 colour/gas etc. products which may be detected by methods
9 known to those skilled in the art.

10

11 Application Three

12

13 As well as providing packaging indicators which respond to
14 temperature, it would be desirable to provide indicators
15 which respond also to the passage of time, thereby
16 recognising that certain categories of product, such as
17 foodstuffs, will go off with time even if maintained at
18 their optimum temperature.

19

20 The present invention therefore provides in one embodiment
21 an indicator to show time specific changes which contains a
22 water holding medium. This may be an inert material (like
23 for example sponge) although gelling agents are preferred.
24 Examples include proteins (like gelatine), synthetic
25 polymers like 'hydrogel', polysaccharides, and similar
26 materials. Polysaccharides are preferred because of their
27 effectiveness and relatively low cost.

28

29 Example Nine

30

31 Polysaccharide solutions containing one or more
32 polysaccharide were prepared and poured into wells to make

1 strips of gel. The gels were allowed to set and the
2 following experiments were conducted but serve as examples
3 only.

4
5 Type of Gelling Agent

6
7 Many polymers and polysaccharides (e.g. agar, carrageenan,
8 locust bean gum xanthan, waxy-, normal- and high amylose
9 starches and gelatine) were investigated for their gel
10 strength and ability to support molecular diffusion of water
11 soluble dyes. These polymers were dissolved in water and
12 dilute alkali solutions (since the diffusion was often based
13 on a pH indicator diffusing through the gel and colouring as
14 it diffused). The polymers were stored at freezing,
15 refrigeration and ambient temperatures and their properties
16 were investigated.

17
18 Agar and carrageenan (singly or in combination) were
19 preferred media for refrigeration and room temperature use.
20 For sub zero temperatures, locust bean gum and xanthan were
21 preferred (singly or in combination), as they did not
22 exhibit extensive syneresis as a consequence of freeze-thaw
23 cycles.

24
25 Effects of gel strip concentration and dimensions

26 Polysaccharide solutions were made with 1,2,3,4 and 5%
27 polymer in water and 1% sodium bicarbonate (heating is
28 usually required). The solutions were poured into small
29 plastic troughs which were 0.5, 1.0, 2.0 or 4.0mm deep, 0.5,
30 1cm, 1.5 or 2cm wide and 5cm long. Results are shown in the
31 following tables:

39

- 1 Table 5 - Agar concentration and phenol red
 2 diffusion at different strip thickness

Agar conc	Thickness (mm)			
	0.5	1	2	4
1	2.663	2.375	1.95	2.625
2	2.513	2.2	2.613	2.375
3	2.4	2.213	2.413	2.363
4	2.013	1.975	2.138	2.375
5	2.163	2.213	2.275	3.038

- 3
 4 Table 6 - Agar concentration and cresol red
 5 diffusion at different strip thickness

Agar conc	Thickness (mm)			
	0.5	1	2	4
1	2.538	2.888	2.5	2.588
2	2.213	2.5	2.4	2.588
3	2.25	2.063	2.225	2.413
4	1.788	1.738	1.775	1.713
5	2.06	1.975	1.725	1.875

- 6
 7 Table 7 - Agar concentration and phenol red
 8 diffusion at different strip sizes

Strip size	Thickness							
	0.5				1			
	1	2	3	4	1	2	3	4
Agar conc 1	2.75	2.8	3	2.1	2.5	2.5	2.4	2.1
2	2.55	2.65	2.5	2.35	2.75	2.35	1.9	1.8
3	2.65	2.65	2.4	1.9	2.35	2.25	2	2.25
4	2.25	2.1	1.9	1.8	2.25	2.25	1.65	1.5
5	2.5	2.25	1.9	2	2.3	2.3	2.25	2

40

	Thickness							
	2				4			
Strip size	1	2	3	4	1	2	3	4
Agar conc 1	2.2	2.1	1.55	2	2.6	2.7	2.6	2.6
2	3	2.5	2.2	2.75	2.5	2.45	2.5	2.05
3	2.75	2.25	2.5	2.15	2.5	2.5	2.05	2.4
4	2.25	2.1	2.1	2.1	2.75	2.4	2.25	2.1
5	2.35	2.35	2.5	1.9	3.25	3.25	2.9	2.75

1

2 Table 8 - Agar concentration and cresol red diffusion at
 3 different strip sizes

	Thickness							
	0.5				1			
Strip size	1	2	3	4	1	2	3	4
Agar conc 1	2.55	2.55	2.55	2.5	3.15	2.9	2.75	2.75
2	2.6	2.35	2.1	1.8	2.75	2.75	2.45	2.05
3	2.3	2.2	2.5	2	2	2.1	2	2.45
4	2.2	1.75	1.65	1.55	2	1.8	1.65	1.5
5	2.1	2.1	2	2.05	2.15	1.85	1.9	2

4

	Thickness							
	2				4			
Strip size	1	2	3	4	1	2	3	4
Agar conc 1	2.65	2.6	2.5	2.25	2.75	2.7	2.55	2.35
2	2.65	2.5	2.35	2.1	2.7	2.5	2.75	2.4
3	2.55	2.35	2	2	2.7	2.25	2.6	2.1
4	2.1	1.9	1.5	1.6	1.8	1.75	1.55	1.75
5	1.85	1.75	1.65	1.65	2	1.8	1.85	1.85

5

- 1 Table 9 - Incubation time and phenol red diffusion
 2 of different strip thickness of agar concentrations

		Thickness (mm)			
Agar conc	days	0.5	1	2	4
1%	1	0.5	0.5	0.5	0.5
	2	1	1	1	1
	3	1.5	1.5	1.5	1.5
	4	2.15	2.163	1.575	2.133
	5	2.663	2.375	1.95	2.625

3

		Thickness (mm)			
Agar conc	days	0.5	1	2	4
2%	1	0.5	0.5	0.5	0.5
	2	1.3	1.225	1.463	1.225
	3	1.738	1.7	2.15	1.55
	4	2.088	2.05	2.4	2.013
	5	2.513	2.2	2.613	2.375

4

		Thickness (mm)			
Agar conc	days	0.5	1	2	4
3%	1	0.5	0.5	0.5	0.5
	2	1	1	1	1
	3	1.513	1.588	1.563	1.475
	4	1.813	1.913	2.138	1.963
	5	2.4	2.213	2.413	2.363

5

		Thickness (mm)			
Agar conc	days	0.5	1	2	4
4%	1	0.5	0.5	0.5	0.5
	2	0.988	1.15	1.288	1.288
	3	1.5	1.55	1.675	1.75
	4	1.888	1.888	2.125	2.113
	5	2.013	1.975	2.138	2.375

		Thickness (mm)			
Agar conc	days	0.5	1	2	4
5%	1	0.5	0.5	0.5	0.5
	2	1.138	1.313	1.225	1.875
	3	1.588	1.613	1.763	2.525
	4	1.913	2.175	1.938	2.7
	5	2.163	2.213	2.275	3.038

1

2 Table 10 - Incubation time and cresol red diffusion
3 of different strip thickness of agar at different
4 concentrations

		Thickness (mm)			
Agar conc	days	0.5	1	2	4
1%	1	0.5	0.5	0.5	0.5
	2	1	1	1	1
	3	1.5	1.5	1.5	1.5
	4	2	2.038	1.95	1.98
	5	2.538	2.888	2.5	2.583

5

		Thickness (mm)			
Agar conc	days	0.5	1	2	4
2%	1	0.5	0.5	0.5	0.5
	2	1.25	1.3	1.238	1.35
	3	1.575	1.875	1.913	1.963
	4	2.05	2.3	2.325	2.363
	5	2.213	2.5	2.4	2.588

6

7

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11

12

43

		Thickness (mm)			
Agar conc	days	0.5	1	2	4
3%	1	0.5	0.5	0.5	0.5
	2	1	1	1	1
	3	1.363	1.25	1.5	1.588
	4	2.05	1.95	1.788	2.063
	5	2.25	2.063	2.225	2.413

1

		Thickness (mm)			
Agar conc	days	0.5	1	2	4
4%	1	0.5	0.5	0.5	0.5
	2	0.625	1	0.825	0.813
	3	0.838	1.1	1.15	1.163
	4	1.363	1.313	1.463	1.638
	5	1.788	1.738	1.775	1.713

2

		Thickness (mm)			
Agar conc	days	0.5	1	2	4
5%	1	0.5	0.5	0.5	0.5
	2	1.1	1.05	0.875	0.888
	3	1.438	1.463	1.163	1.05
	4	2.05	1.863	1.563	1.863
	5	2.06	1.975	1.725	1.875

3

4 Table 11 - Diffusion of phenol red at different strip
 5 sizes and thickness of Gum locust bean and Gum xanthan

		Thickness							
		0.5				1			
Strip size		1	2	3	4	1	2	3	4
Agar conc 1	2	1.65	1.25	1.25	2.25	1.15	1	1	
2	2	1.25	1.25	1	1.75	1.4	1.15	1.25	

6

	Thickness							
	2				4			
Strip size	1	2	3	4	1	2	3	4
Agar conc 1	1.75	1.4	1	1	2	1.65	1.25	1.25
2	1.25	1	1	1	1.1	1	1	1

1

2 Table 12 - Diffusion of cresol red at different strip
 3 sizes and thickness of Gum locust bean and Gum xanthan

	Thickness							
	0.5				1			
Strip size	1	2	3	4	1	2	3	4
Agar conc 1	3	2.25	1	1	1.1	1.1	1	1
2	1.75	1.15	1.15	1.15	1.6	1.6	1.4	1.35

4

	Thickness							
	2				4			
Strip size	1	2	3	4	1	2	3	4
Agar conc 1	1.2	1.15	1.15	1.15	1.4	1.1	1.1	1
2	1	1	1	1	1	1	1	1

5

6 Table 13 - Diffusion of phenol red and incubation
 7 time of different strip thickness with different
 8 carrageenan conc.

		Thickness (mm)			
Carr. conc	days	0.5	1	2	4
1%	1	0.5	0.5	0.5	0.5
	2	1	1.238	1.088	1.175
	3	1.35	1.238	1.175	1.275
	4	1.763	1.438	1.475	1.75
	5	2.05	1.913	1.738	1.75

45

		Thickness (mm)			
Carr. conc	days	0.5	1	2	4
2%	1	0.5	0.5	0.5	0.5
	2	0.9	0.938	1	0.888
	3	1.375	1.325	1.613	1.275
	4	1.925	1.55	1.663	1.525
	5	2.013	1.638	1.85	1.525

1

		Thickness (mm)			
Carr. conc	days	0.5	1	2	4
3%	1	0.5	0.5	0.5	0.5
	2	0.75	0.988	0.925	0.788
	3	1.638	1.213	0.988	1.15
	4	1.763	1.313	1.188	1.163
	5	1.975	1.475	1.288	1.188

2

		Thickness (mm)			
Carr conc	days	0.5	1	2	4
4%	1	0.5	0.5	0.5	0.5
	2	0.8	0.75	0.888	0.65
	3	1.5	1.1	1.625	1.13
	4	1.538	1.25	1.838	1.25
	5	1.988	1.588	1.975	1.25

3

		Thickness (mm)			
Carr. conc	days	0.5	1	2	4
5%	1	0.5	0.5	0.5	0.5
	2	0.638	0.613	0.525	0.563
	3	0.825	0.938	0.8	0.675
	4	1.088	1.125	0.9	0.9
	5	1.088	1.125	0.9	0.9

4

- 1 Table 14 - Diffusion of cresol red and incubation
 2 time of different strip thickness with different
 3 carrageenan conc.

		Thickness (mm)			
Carr. conc	days	0.5	1	2	4
1%	1	0.5	0.5	0.5	0.5
	2	0.975	1	1.1	1.238
	3	1.275	1.2	1.3	1.325
	4	1.638	1.363	1.4	1.538
	5	1.85	1.725	1.522	1.563

		Thickness (mm)			
Carr. conc	days	0.5	1	2	4
2%	1	0.5	0.5	0.5	0.5
	2	1.388	1.313	1.125	1
	3	1.65	1.563	1.263	1.35
	4	1.913	1.813	1.725	1.488
	5	2.025	1.863	1.938	1.65

		Thickness (mm)			
Carr. conc	days	0.5	1	2	4
3%	1	0.5	0.5	0.5	0.5
	2	1.063	1.063	1.125	1.125
	3	1.063	1.063	1.2	1.188
	4	1.375	1.275	1.463	1.188
	5	1.375	1.338	1.463	1.25

47

		Thickness (mm)			
Carr conc	days	0.5	1	2	4
4%	1	0.5	0.5	0.5	0.5
	2	0.963	1.088	0.813	1.038
	3	0.963	1.163	1.013	0.963
	4	1.288	1.288	1.1	1.1
	5	1.788	1.288	1.125	1.138

1

		Thickness (mm)			
Carr. conc	days	0.5	1	2	4
5%	1	0.5	0.5	0.5	0.5
	2	0.863	0.65	0.6	0.55
	3	0.963	0.85	0.713	0.625
	4	1.175	1.363	0.85	0.75
	5	1.175	1.363	0.85	0.75

2

3 Table 15 - Diffusion of phenol red and carrageenan
 4 concentration at different strip sizes with different
 5 thickness

	Thickness							
	0.5				1			
Strip size	1	2	3	4	1	2	3	4
Carr. conc	3.15	2.15	1.45	1.45	1.9	2.5	1.75	1.5
1	2.9	2.15	1.5	1.5	2.25	1.6	1.35	1.35
2	2.75	1.9	1.85	1.4	2.25	1.4	1.25	1
3	2.9	2.15	1.4	1.5	1.85	1.5	1.5	1.5
4	1.75	0.9	0.9	0.8	1.65	1.1	0.9	0.8
5						5		

6

7

8

9

10

	Thickness							
	2				4			
Strip size	1	2	3	4	1	2	3	4
Carr. Conc 1	1.9	1.5	1.9	1.65	1.75	1.75	1.75	1.75
2	2	2	1.75	1.65	2.25	1.5	1.5	0.85
3	1.6	1.35	1.1	1.1	1.5	1	1.25	1
4	3	2.15	1.5	1.25	1.65	1.35	1	1
5	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9

Table 16 - Diffusion of cresol red and carrageenan concentration at different strip sizes with different thickness

	Thickness							
	0.5				1			
Strip size	1	2	3	4	1	2	3	4
Carr. conc 1	2.5	2.1	1.65	1.15	1.8	1.9	1.6	1.6
2	2.75	2.25	1.7	1.4	2.5	1.65	1.65	1.65
3	2.25	1.15	1.05	1.05	1.85	1.1	1.1	1
4	2	1.6	1.25	1.25	2	1	1	1.15
5	1.65	1.25	0.9	0.9	2	1.15	1.15	1.15

	Thickness							
	2				4			
Strip size	1	2	3	4	1	2	3	4
Carr. conc 1	1.6	1.5	1.5	1.5	1.75	1.5	1.5	1.5
2	2.5	1.75	1.75	1.75	2.25	1.55	1.4	1.4
3	2.15	1.4	1.15	1.15	2	1	1	1
4	1.5	1.1	0.9	1	1.55	1	1	1
5	1	0.8	0.8	0.8	1.05	0.65	0.65	0.65

1 By way of example, Figure 7 shows the results of table 5 in
2 graph form.

3

4 The above results as a whole show that:

5

6 Diffusion of water soluble dyes from one end of the gel to
7 the other is slower as concentration is increased.

8

9 Depth or width, for the same amount of dye applied at one
10 end, do have some effect on the rate of dye diffusion. As
11 the depth and width increase the rate of diffusion is
12 reduced.

13

14 Length is very important as the diffusion occurs over many
15 days. Typically it takes 5 days for dye dispersed in a
16 liquid fat (e.g. 1% with respect to cresol red or 1% with
17 respect to phenol red) to diffuse from one end to the other
18 of a 3cm gel strip (2mm deep and 0.5cm wide) prepared in 1%
19 sodium bicarbonate solution and stored at 5°C. Hence time
20 dependence and self life dependence could be determined
21 using this approach.

22

23 At higher temperatures, the rate of diffusion is increased.
24 For example, for the above experiment it would occur at 3
25 rather than 5 days if stored at 25°C.

26

27 Geometry is not a rate limiting effect on diffusion, as the
28 gels may be stored under any orientation and the diffusion
29 occurs at the same rate. Spirals of the matrix have also
30 been made and work very effectively.

31

1 The gels prepared in 1% sodium bicarbonate (2% with respect
2 to polysaccharide) were stored at refrigeration temperatures
3 for up to 16 weeks and no microbiological storage was
4 detected. The gels must, however, not be allowed to dry out.

5

6 A modification of these gels strips has been to incorporate
7 gelatinised maize starch with agar gels in the ratios from
8 25:75% to 75:25% (although any other ratios are not excluded
9 nor combinations of gels containing one or more hydrolysable
10 material) with a total solids concentration of 0.5 to 5%.
11 Before the gels set, thermostable alpha-amylase (e.g. 0.1 to
12 1mg ml) was added. Thin strips were cut (as above) and were
13 stored at room temperature. It was found that the rate of
14 diffusion could be increased where the enzyme was present as
15 it slowly hydrolysed the starch component of the matrix.
16 Other polysaccharides with other appropriate hydrolytic
17 enzymes may be used (e.g. xanthan and xanthanase, pectin and
18 pectinase etc.).

19

20 Figure 4 shows a practical example of an indicator in plan
21 view and side elevations. Indicator 30 comprises a gel
22 strip 31 upon which is immobilised water-soluble, lipid-
23 insoluble gel in a matrix of frozen lipid 32.

24

25 Application four - Triggerable indicators.

26

27 When manufacturing the product as described in the second
28 application above, the sensors as made must be transported
29 below the trigger temperature. This can make manufacture
30 difficult. To avoid this problem, the lipid phase can be
31 immobilised as a solid or liquid in a discrete compartment.
32 When activation is required, the product is cooled to below

the trigger temperature whereupon the lipid (now solid) containing compartment is ruptured. Mechanical rupture has proved very successful although other triggering processes are not ruled out. When the temperature exceeds the melting point of the lipid, it melts and moves towards the agar phase and colour development occurs.

Example Ten

Agar (1%) containing sodium bicarbonate (1%) was prepared as described above (3). Oleic acid containing cresol red or phenol red indicator (1%) was sealed in a small plastic or metal pouch and placed in a ring cut within the agar. The temperature was cooled to 5°C whereupon the pouch was pierced. The contents remained in the pouch until the temperature exceeded 13.4°C whereupon the lipid (containing cresol red) began to run out of the pouch and into the agar phase and colour developed.

In general, this application uses lipid and gel phases which are partitioned with barriers that are broken after cooling and the product becomes active. We have built many designs where the trigger is:

Mechanically ruptured by physical force (pressure, rotation etc.)

Activated by material contraction upon cooling

Activated by enzymatic hydrolysis of lipid or gelling phases or a separating phase.

1 Activated by ripping out a barrier or film.

2

3 Activated by hydrating the gelling phase (pregelatinised
4 starch is especially valuable) or a separate barrier phase

5

6 Many other activation processes are possible and will be
7 readily apparent to one skilled in the art.

8

9 Application Five

10

11 These technology allow the interesting idea of preparing
12 barcodes which have an appearance which is time-temperature
13 sensitive. Once the time-temperature transition has taken
14 place, probably when the product in question has expired,
15 the bar code reading changes. For example, individual lines
16 or the whole bar code disappear. Alternatively colour may
17 appear. This allows the creation of a system whereby
18 expired product cannot be bar-code read or can give a
19 different signal to a bar code reader allowing, for example,
20 defectively stored supplies to be immediately identified and
21 not accepted. Example constructions are as follows:

22

23 Lipid melting has been used to reveal or disguise part or
24 all of the barcode.

25

26 The bars of the bar code have been printed with thermo-
27 sensitive materials like lipids which, melt at a defined
28 temperature and reveal temperature exposure.

29

30 Lipid containing a water soluble reactant has been placed in
31 close contact with a thin gel phase above or below the
32 barcode itself. Upon melting, the lipid makes contact with

1 the gel and colour development occurs. This leads to the
2 loss of visibility of the discrete lines.

3

4 The lipid may be replaced with other melting materials.

5

6 The barcode may be printed directly onto the product or
7 packaging material. When the product has been heated up
8 above the melting point of the material it melts and the
9 code is lost.

10

11 Figure 5 shows an example triggerable indicator which can be
12 used with the bar code concept. Indicator 40 has a PIP, for
13 example a lipid block 41 which contains, as before, a water-
14 soluble, lipid-insoluble dye. When it melts, it may contact
15 agar block 42 giving a visual colour change as described
16 above. Another agar block 43 is separated from the lipid
17 block 41 by a gate 44. The gate may have a plurality of
18 bars which block corresponding gaps in an adjacent wall,
19 meaning that the gate has to move only the width of one bar
20 to allow lipid/agar mixing. The gate is activated by a
21 locking thermostat 45 which may, for example, by a
22 bimaterial strip which bends with temperature and,
23 optionally, a latch mechanism. Warming the device to a
24 temperature causes the lipid block to melt giving an
25 indication when the PR interacts with the first agar block
26 42. At a second temperature the thermostat allows the lipid
27 block 41 to interact with agar block 43. The benefit of
28 this device is that it can indicate both a short high
29 temperature event (colour change in agar block 42) and have
30 the capacity to indicate a longer high temperature event
31 (through diffusion of dye in agar block 43).

32

1 Key benefits of the invention as described herein are that
2 it provides a permanent and irreversible record that a
3 temperature-time event has occurred. The technology can be
4 activated at the point of manufacture or post manufacture by
5 for example a consumer. This has the added advantage in that
6 the products can be manufactured at ambient temperatures if
7 required and shipped as such rather than under
8 refrigeration.

9

10 Figure 6 shows a cross-section through a further embodiment
11 of the present invention. Indicator 50 comprises a cylinder
12 51 filled with a lipid 52 which contracts linearly with
13 decrease in temperature. Change in volume of the lipid 52
14 drives a piston 53, the motion of which is opposed by a
15 spring 54. The piston is attached by a joining member 55 to
16 a card 56 which can be viewed through a window 57 in a
17 further card 58. At low temperature, one part of card 56 is
18 visible. At high temperature, the lipid expands, and the
19 piston moves, lining the window 57 up with a region of card
20 56 which displays a message, or indicates a colour, to show
21 that a particular temperature has been exceeded. A ratchet
22 and pawl may be added to the piston in order to make the
23 change in indication irreversible. Card 56 may simply be a
24 bicoloured card, with e.g. green (indicating "safe" food
25 product) visible at low temperatures and red (indication
26 "hazardous" food) visible at high temperatures.

27

28 By using these time-temperature indicators on products,
29 consumers will be able to verify that produce they purchase
30 has been stored correctly prior to their purchase and will
31 be able to check they look after it properly and do not use
32 it once it is no longer fit. Manufacturers, distributors

1 and retailers will be able to use the time-temperature
2 indicators for internal quality control and quality
3 assurance and will also better trust that materials
4 protected by this technology have been supplied to them in
5 the correct conditions with all due care. The bar code
6 concept allows rapid verification of the quality of
7 supplies.

8

9 As the invention can provide a dramatic visible change, it
10 will give clear indication to consumers and, as it may be
11 constructed of edible materials, it has the benefit of being
12 able to be attached to actual fresh product directly instead
13 of merely to its packaging. It will also therefore be
14 considered safe and natural by consumers.

15

16 Further modifications and variations will be clear to one
17 skilled in the art and may be made within the scope of the
18 invention herein disclosed.

CLAIMS

1. A thermal history indicator for attachment to goods, the indicator comprising a temperature sensitive material selected to melt at a predetermined temperature; wherein melting of the temperature sensitive material leads to provision to the user of an indication that the temperature of the indicator has exceeded the predetermined temperature.
2. A thermal history indicator as claimed in Claim 1 wherein the temperature sensitive material is edible.
3. A thermal history indicator as claimed in Claim 1 or Claim 2 wherein the temperature sensitive material is a lipid.
4. A thermal history indicator as claimed in any preceding Claim wherein the temperature sensitive material provides a visual image through its shape and which melts at the particular temperature, thereby losing its shape, destroying the visual image and thereby indicating that the particular temperature has been exceeded.
5. A thermal history indicator as claimed in any preceding Claim wherein the temperature sensitive material is mounted on a support, the support being adapted for mounting on goods.
6. A thermal history indicator as claimed in any of Claims 1 to 4, the indicator having a chamber within which the

1 temperature sensitive material is held, the chamber
2 being adapted such that the temperature sensitive
3 material obscures a visual indicator and configured
4 such that melting of the temperature sensitive material
5 results in the visual indicator becoming visible.
6

7 7. A thermal history indicator as claimed in Claim 6
8 wherein the chamber is hemispherical and adapted so
9 that the temperature sensitive material flows from the
10 top to the bottom of the hemispherical chamber on
11 melting.
12

13 8. A thermal history indicator as claimed in any of Claims
14 1 to 3 wherein the temperature sensitive material has a
15 primary reagent immobilised therein; the primary
16 reagent is released upon melting of the temperature
17 sensitive material and the released primary reagent
18 provides an indication that the particular temperature
19 has been exceeded.
20

21 9. A thermal history indicator as claimed in Claim 8
22 wherein the temperature sensitive material is a lipid,
23 the primary reagent is a water-soluble dye and the
24 released water-soluble dye forms a colour on contact
25 with water in the goods to which the indicator is
26 affixed, the formation of the colour leading to a
27 visual indication that the particular temperature has
28 been exceeded.
29

30 10. A thermal history indicator as claimed in Claim 8
31 having a secondary phase located so that when the
32 temperature sensitive material melts, the primary

1 reagent comes into contact with the secondary phase,
2 wherein contact between the primary reagent and the
3 secondary phase leads to an indication that the
4 particular temperature has been exceeded.

5

6 11. A thermal history indicator as claimed in Claim 10
7 wherein the primary reagent interacts with the
8 secondary phase itself in such a way as to produce a
9 colour change.

10

11 12. A thermal history indicator as claimed in Claim 10
12 wherein the secondary phase has a secondary reagent
13 held therein, wherein the first reagent and secondary
14 reagent react giving a product which provides a visual
15 indication.

16

17 13. A thermal history indicator as claimed in Claim 12
18 wherein the first and secondary reagents are, in either
19 order, an enzyme and a substrate for the enzyme.

20

21 14. A thermal history indicator as claimed in any of Claims
22 10 to 13 wherein the temperature sensitive material and
23 the secondary phase are separated by a physical gap.

24

25 15. A thermal history indicator as claimed in any of Claims
26 10 to 13 wherein the temperature sensitive material and
27 the secondary phase are separated by a temperature
28 sensitive barrier.

29

30 16. A thermal history indicator as claimed in Claim 15
31 wherein the temperature sensitive barrier has a gate
32 which is opened by a thermostat.

- 1
- 2 17. A thermal history indicator as claimed in Claim 15 or
- 3 Claim 16 wherein the temperature sensitive barrier is a
- 4 layer of material which melts at a particular
- 5 temperature.
- 6
- 7 18. A thermal history indicator as claimed in any of Claims
- 8 10 to 13 wherein the temperature sensitive material and
- 9 the secondary phase are separated by a physical barrier
- 10 which can be broken and thereby made permeable by a
- 11 user.
- 12
- 13 19. A thermal history indicator as claimed in any of Claims
- 14 10 to 18 wherein the indicator has a means for urging
- 15 molten temperature sensitive material into contact with
- 16 the secondary phase.
- 17
- 18 20. A thermal history indicator as claimed in any of Claims
- 19 10 to 19 wherein the primary reagent diffuses through
- 20 the secondary phase, thereby producing a temperature
- 21 indication that varies with time.
- 22
- 23 21. A thermal history indicator as claimed in any of Claims
- 24 8 to 20 wherein the primary reagent is a water-soluble
- 25 dye.
- 26
- 27 22. A data encoding image comprising a thermal history
- 28 indicator as claimed in any preceding Claim arranged
- 29 such that the data encoded by the data encoding image
- 30 changes when the particular temperature is exceeded.
- 31

1 23. A data encoding image as claimed in Claim 22 wherein
2 the data encoding image is a bar code.

3

4 24. A temperature history indicator comprising a cylinder,
5 a piston and an indicator which can be viewed through a
6 window, the cylinder having therein a material that
7 changes volume with temperature thereby driving the
8 piston, the piston being linked to the indicator such
9 that motion of the piston is coupled to motion of the
10 indicator, wherein motion of the indicator changes the
11 part of the indicator which can be seen through the
12 window, wherein a first portion of the indicator can be
13 viewed through the window at a first temperature and a
14 second portion of the indicator can be viewed through
15 the window at a second temperature, the first and
16 second portions of the indicator having visually
17 different information thereon and thereby indicating
18 that a temperature change has taken place.

19

20 25. A temperature history indicator as claimed in claim 24
21 adapted so that motion of the piston is irreversible.

22

23 26. An indicator for providing temperature sensitive visual
24 images on goods, the indicator comprising lipid formed
25 into a visual image, the lipid being selected to melt
26 above a particular temperature, thereby destroying the
27 visual image.

1/7

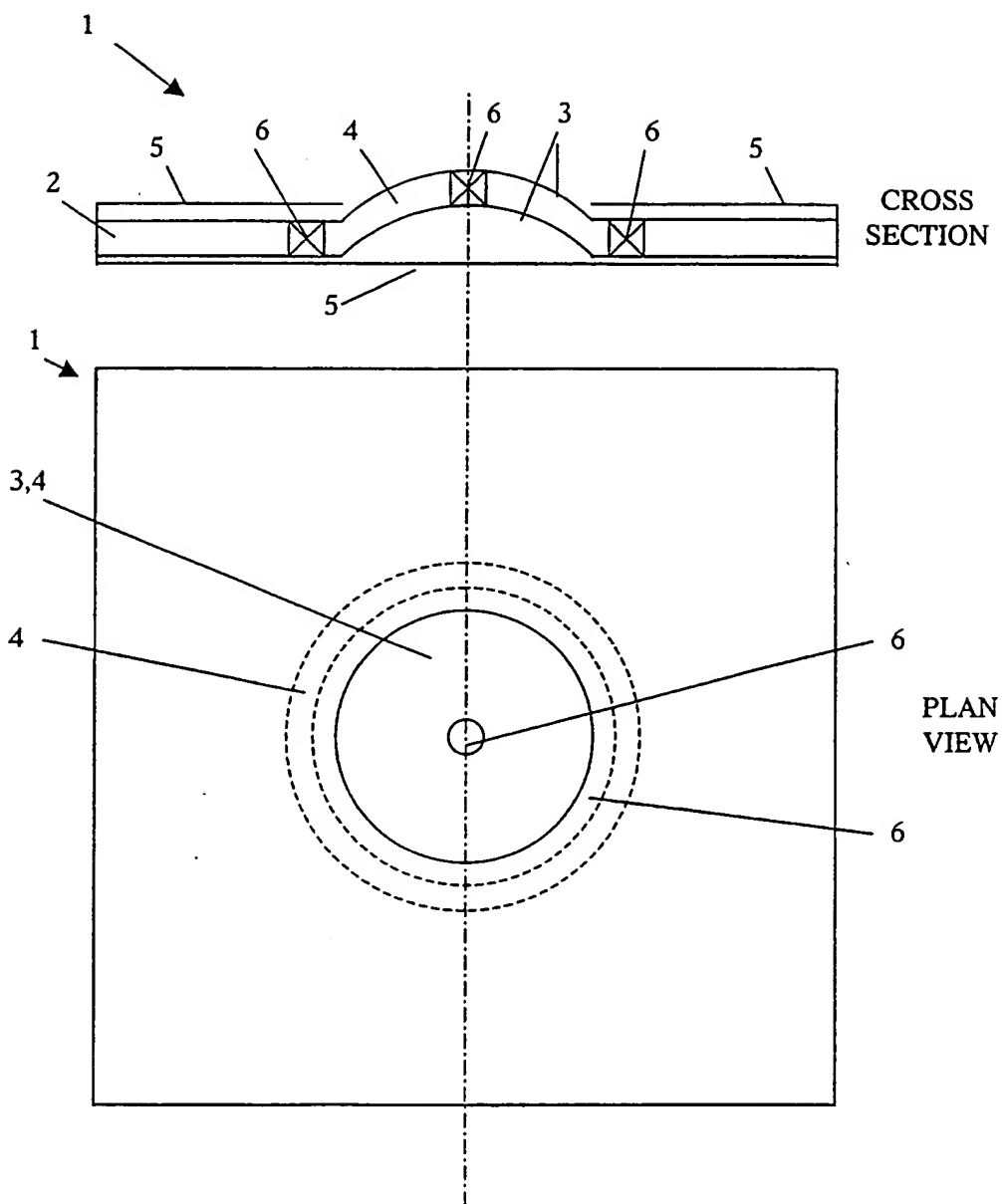


FIGURE 1

2/7

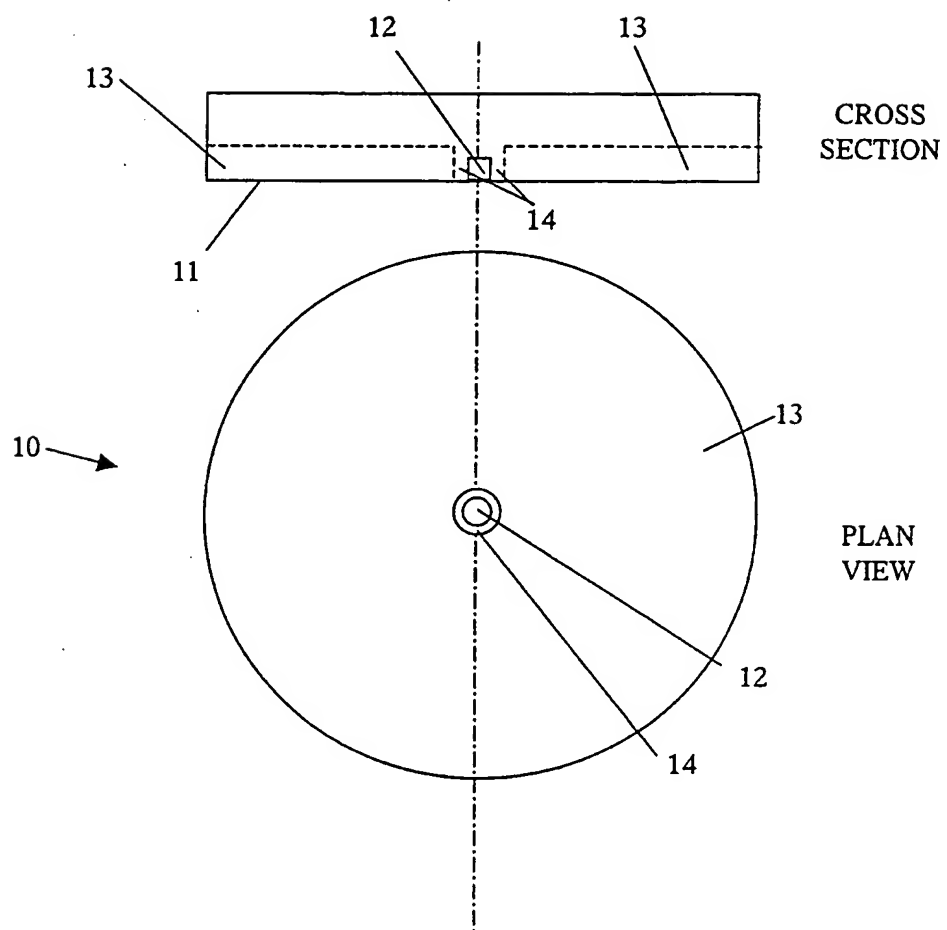


FIGURE 2

3/7

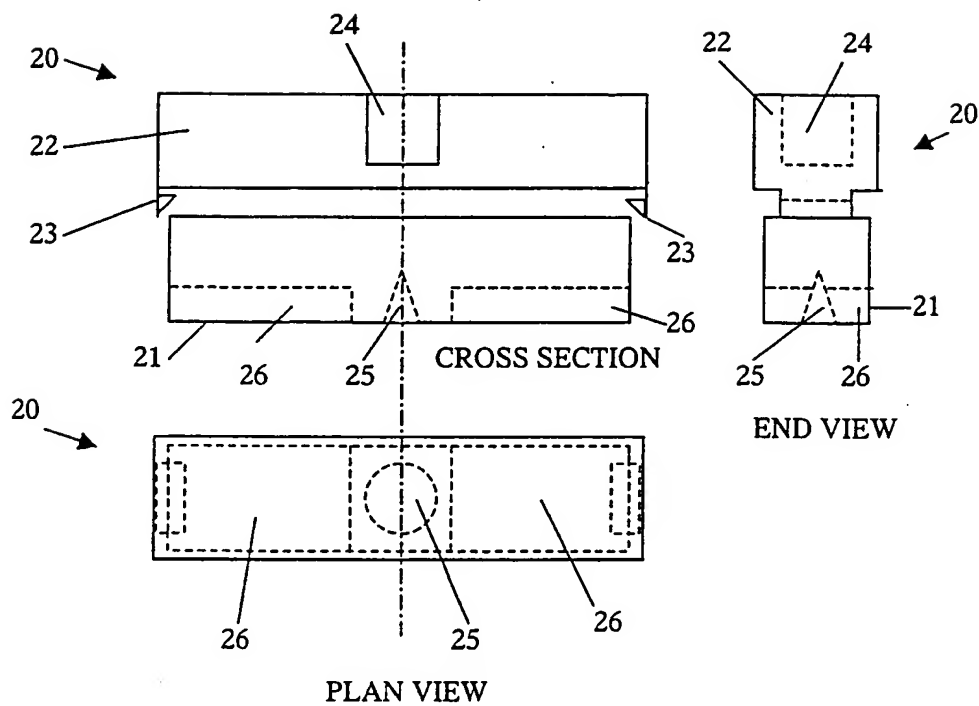


FIGURE 3

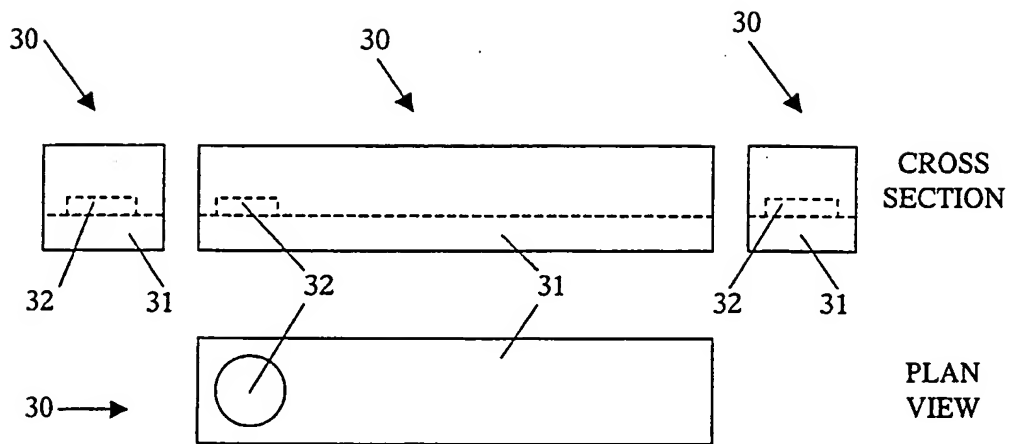
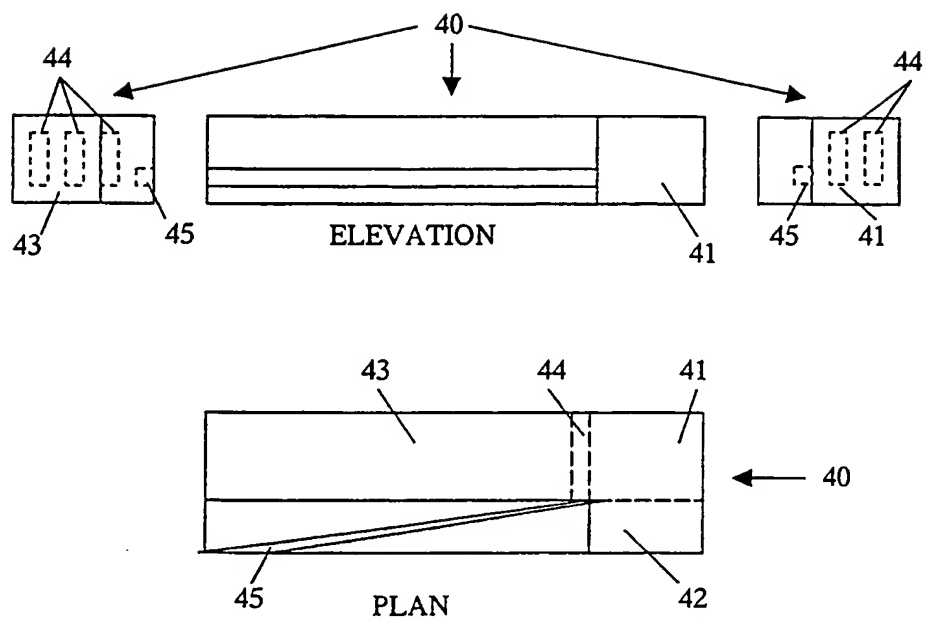


FIGURE 4

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**FIGURE 5**

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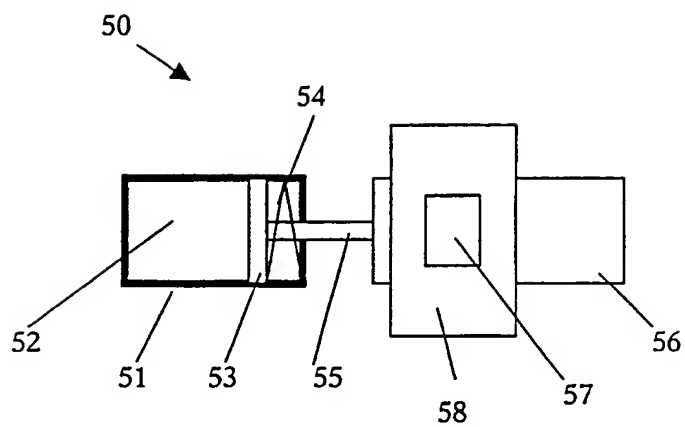
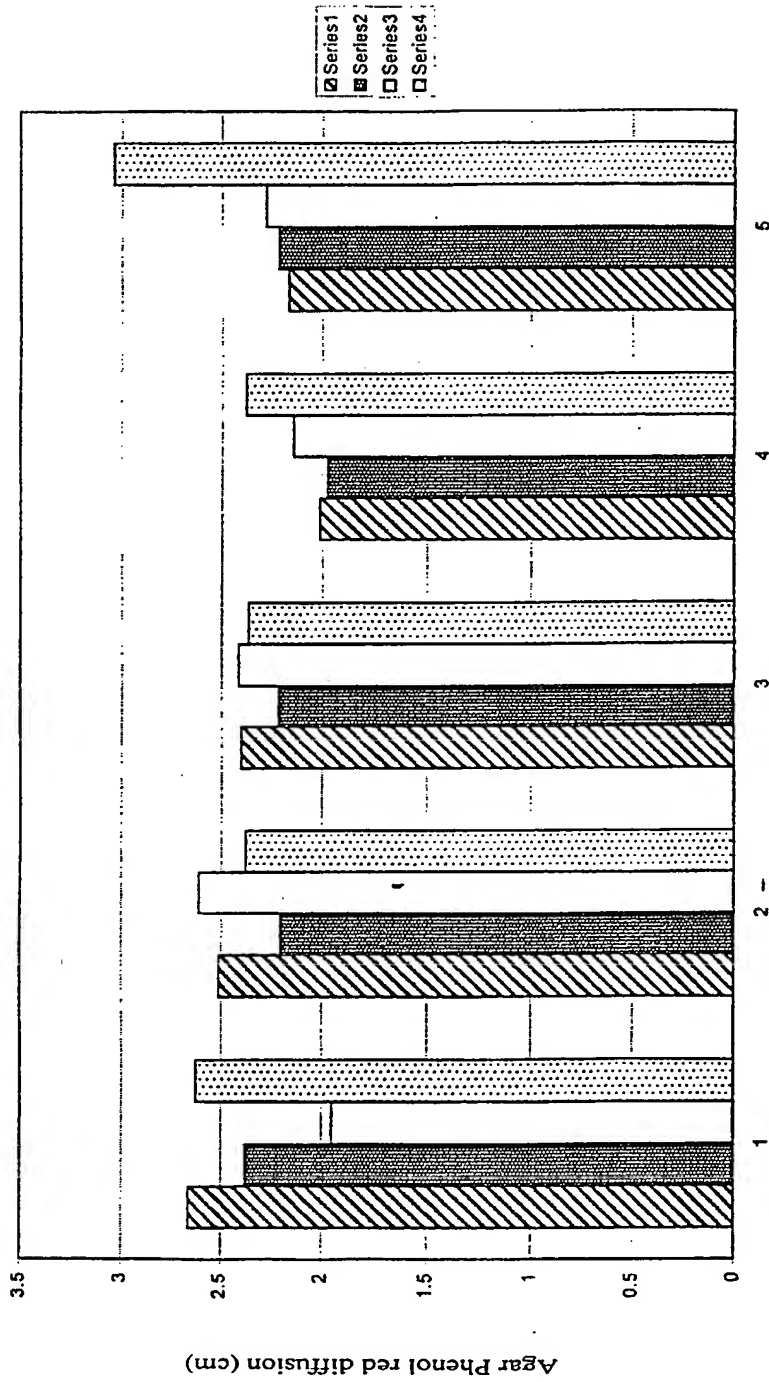


FIGURE 6

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Agar concentration (%) at different strip thickness

FIGURE 7

INTERNATIONAL SEARCH REPORT

Inter- national Application No

PCT/GB 00/00398

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 G01K11/06 G01K3/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 G01K G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	US 2 553 369 A (S. HOFFMAN) 15 May 1951 (1951-05-15) the whole document	1,2,5
X	WO 92 14998 A (RAMET JEAN PAUL ; FANNI JACQUES (FR)) 3 September 1992 (1992-09-03) the whole document	1,2,4, 10,13
	-/-	



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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Date of the actual completion of the international search

9 May 2000

Date of mailing of the international search report

17/05/2000

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INTERNATIONAL SEARCH REPORT

Internal Application No

PCT/GB 00/00398

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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